

# Fe clusters on Ni and Cu: size and shape dependence of the spin moment

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We present ab-initio calculations of the electronic structure of small Fe clusters (1-9 atoms) on Ni(001), Ni(111), Cu(001) and Cu(111) surfaces. Emphasis is given on the spin moments, and their dependence on cluster size and shape. We derive a simple quantitative rule, which relates the moment of each Fe atom linearly to its coordination number. Thus, for an arbitrary Fe cluster the spin moment of the cluster and of the individual Fe atoms can be readily found if the positions of the atoms are known.

Small atomic clusters on surfaces constitute an extremely interesting subject, as their electronic structure lies in the transition from the behaviour in bulk to that of free molecules or atoms. In particular, the electronic structure is characteristic of the cluster in that it depends on the cluster atoms, shape, size, and orientation, as well as on the substrate material on which the cluster is deposited. Thus it is *terra incognita* for the electronic properties. Moreover, since they are not hidden in the bulk, such structures are directly accessible by a number of experimental techniques, such as scanning tunneling microscopy, x-ray magnetic circular dichroism, photoemission, etc.

In the area of magnetism, small clusters of magnetic atoms on surfaces are expected to experience an enhancement of the magnetic properties. As the cluster size decreases and the average coordination of the atoms becomes smaller, the decreased hybridisation of the atomic wavefunctions should lead to more pronounced magnetic effects. Such trends with cluster size have been monitored in recent experimental works; for example, using x-ray magnetic circular dichroism, Lau and co-workers [1] have focused on Fe/Ni(001) systems, while Gambardella and collaborators [2] have examined Co clusters on Pt(111); and nuclear resonant scattering of synchrotron radiation has been employed for the study of Fe islands on W(110) [3]. Also other techniques, such as perturbed angular correlation [4] or spin-polarized scanning tunneling spectroscopy [5], allow the analysis of magnetic atoms on surfaces in the sub-monolayer regime, giving further impetus to the field.

Similar to the ferromagnetic Fe, Co, and Ni clusters, V, Cr, and Mn clusters should also have a strong intra-atomic exchange field; but, in contrast to the ferromagnetic clusters, their inter-atomic exchange should be antiferromagnetic, and due to competing interactions the resulting magnetic order is in general non-collinear and depends on individual details. Thus it will differ among clusters, and to investigate the individual magnetic order of such clusters is a challenge for both experiment and theory.

But even for homo-atomic and mass-selected clusters it is very difficult to address experimentally the magnetic properties of each one individually, let alone each atom in

a cluster. In many cases just the mean moment of clusters of a particular size or the average mean magnetic moment per atom is found, averaged over an ensemble of clusters of the same size but different shapes. This motivated us to investigate the local and global spin moments of small Fe clusters (up to 9 atoms) of monoatomic height and varying shape and size with a material specific theory of predictive power, namely density functional theory. In this paper we summarise our results by establishing a simple quantitative rule which relates the local spin moment of an Fe atom in the cluster linearly to the coordination number of its nearest neighbour atoms, with little influence of the structure of the atoms in the rest of the cluster. In this way for any arbitrary Fe cluster the spin moment of the cluster and of the individual Fe atoms can be readily found if the positions of the atoms are known. Even if the cluster shapes and sizes are not exactly known experimentally, by making a reasonable assumption of the variation of sizes and shapes the proposed rule allows an estimation of the variation of the total moment across the deposited clusters. Motivated by the work of Lau *et al.* [1] we concentrated our attention on Fe clusters on the (001) and (111) surfaces of the ferromagnetic substrate Ni and the non-magnetic substrate Cu.

First-principles calculations of clusters on surfaces can be computationally quite demanding, considering that such systems break the translational symmetry in all three directions. Most *ab-initio* methods explicitly exploit the translational symmetry and the clusters on surfaces are approximated by huge, computationally expensive supercells which are periodically repeated. So far they have been applied mostly for magnetic adatoms and chains [6]. A breakthrough in the treatment of magnetic clusters was the development of the Green function method of Korringa, Kohn and Rostoker [7, 8] for the embedding of clusters at surfaces. Subsequent applications [9, 10, 11] established this method as a powerful tool.

Our calculations are based on density-functional theory in the local spin-density approximation [13] (LSDA). The Green function method of Korringa, Kohn, and Rostoker (KKR) is employed [8] to determine the spin density and effective potential. Within the method, the

Green function of the perturbed system, *i.e.*, surface plus cluster, is related to the one of the “host” reference system (the clean substrate) by a Dyson equation. In this way the correct host boundary conditions are included automatically in the Green function, thus no supercell construction is needed. In order to allow for a screening of the perturbation induced by the cluster, at least the first neighbouring sites of all cluster atoms were considered in the self-consistency cycle. The angular momentum expansion of the Green functions was truncated at  $l_{\max} = 3$ . Tests have shown that these parameters give reliable results for these systems.

A full-potential approach with the correct description of the atomic cells [14] was used. Since we are focusing here on trend calculations, the atoms in the clusters were situated in the unrelaxed lattice positions, using the LSDA equilibrium lattice parameter of 6.46 au (3.417 Å) for Ni and 6.63 au (3.507 Å) for Cu [15].

The clusters considered on the Ni(001) surface are shown schematically in Figure 1 viewed from the top (all atoms lie on the surface). The view is adapted to surface geometry, meaning that it is rotated by  $45^\circ$  with respect to the in-plane fcc cubic axes. The smallest cluster is a single Fe adatom, while the largest consists of 9 Fe atoms. In each atom, the calculated spin moment is written, and the average (per atom) moment of each cluster is also given. The Fe moment is always ferromagnetically coupled to the Ni substrate moment and to the Fe moments within the clusters. Already at a first glance it is obvious that the average moment of the clusters depends on the cluster size. The single adatom has manifestly the highest moment ( $3.24 \mu_B$ ), while the 9-atom cluster shows a lower average moment of  $2.85 \mu_B$ .

This behaviour is expected on the grounds of hybridisation of the atomic d levels with the neighbours. Atoms in larger clusters have, on the average, higher coordination, thus their d wavefunctions are more hybridised; this leads to lesser localisation and lesser tendency to magnetism.

To pursue this idea further, we tried to correlate the local atomic spin moment to the nearest neighbour coordination of each atom, irrespective of the form or size of the cluster. For instance, let us focus on all Fe atoms which have only one first Fe neighbour, *i.e.*,  $N_c = 1$  (the coordination to the substrate is the same,  $N_s = 4$ , for all Fe atoms). Such atoms appear in the clusters with size 2, 3, 4, 5, and 7; there are, in total, 10 such examples (having excluded cases which are trivially equivalent by symmetry). *All* of them have spin moments ranging in the small interval between  $3.10$  and  $3.13 \mu_B$ . Similarly, for the Fe atoms with two Fe neighbours the spin moment ranges from  $2.91$  to  $2.97 \mu_B$ . Collecting all possible cases, from  $N_c = 0$  (single adatom) to  $N_c = 4$ , we present the results in Figure 1B.

A surprising feature is the almost linear dependence of the spin moment on the coordination number. In the general case, for arbitrary magnetic atoms, this is not

### (A) Moments in Fe clusters at Ni(001) surface

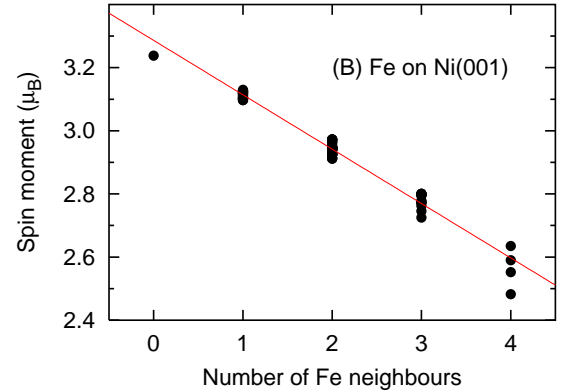
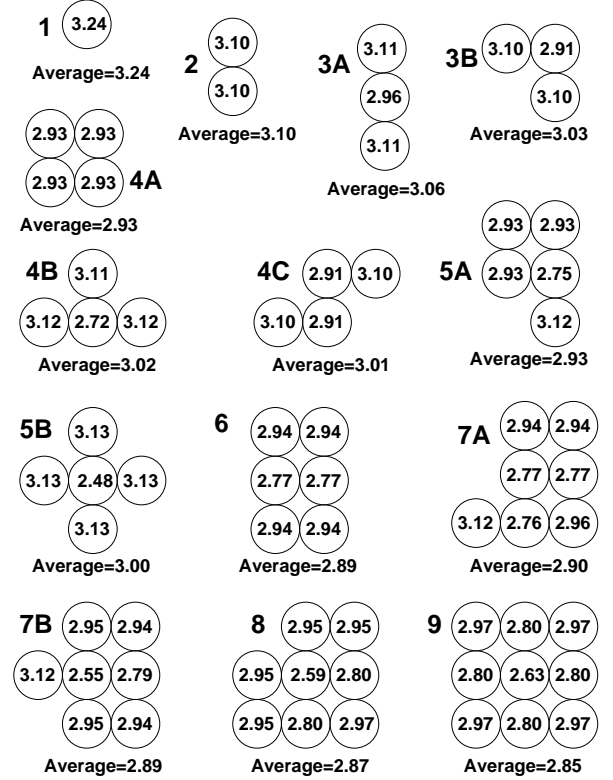


FIG. 1: A: Spin moment (in  $\mu_B$ ) of atoms in 14 different Fe clusters ranging from 1 to 9 atoms on the Ni(001) surface, and average (per atom) moment of the clusters (the view is surface-adapted, *i.e.*, rotated by  $45^\circ$  with respect to the in-plane fcc cubic axes; the clusters are viewed from the top, *i.e.*, all atoms lie on the surface). B: Linear trend for the atomic Fe spin moment as function of the coordination number of nearest Fe neighbours.

expected. For example, Ref. 7 shows a study of the magnetism of small 4d atom clusters on Ag(001). There, it is reported that the susceptibility is highly non-local, resulting even in an increase of the spin moment with increasing coordination. This is related to the larger extent of the 4d wavefunctions compared to the 3d ones of

Fe. In our case, Fe has a strong intra-atomic exchange field, arising from rather localised 3d wavefunctions and their positioning with respect to the Fermi level  $E_F$ . In a non-magnetic picture,  $E_F$  is well within the d virtual bound state, and the non-magnetic density of states at  $E_F$ ,  $n(E_F)$ , is always well above the transition point to the magnetic state: the Stoner criterion  $I \cdot n(E_F) > 1$  (with  $I$  being the exchange integral) is safely fulfilled. Thus, the hybridisation of the 3d levels with the neighbours' wavefunctions does not affect the nonmagnetic  $n(E_F)$  critically. With increasing coordination,  $n(E_F)$  is gradually lowered, and so is the intra-atomic exchange field. The tiny variation of the local moments for Fe atoms with the same nearest neighbour coordination but being in different clusters may arise from intra-cluster interference effects or indirectly via the different polarisation of the substrate.

Preliminary results on Co clusters, for which the 3d virtual bound state is lower in energy, show that this linear behaviour holds to a lesser extent, and much less so for Ni, where the intra-atomic exchange field is even weaker [16]. A similar difference among Fe, Co, and Ni clusters on Ag(001) has been shown in Ref. [11] and [9].

On the other hand, Mn and Cr should have a strong intra-atomic exchange field, but they present tendency for antiferromagnetism or even non-collinear magnetic structures [16]. In this respect, Fe is expected to be perhaps unique among the transition elements in showing such a clear cut linear trend.

Similar is the case of Fe clusters on the more compact Ni(111) substrate. The considered clusters, sized up to 8 atoms, are shown together with the spin moments in Figure 2A. Since the Fe adatom on the (111) surface has only 3 Ni neighbours instead of 4 on the (001) surface, its spin moment is higher than on the (001) surface. On the other hand, the number of Fe neighbours (in-plane) can increase up to  $N_c = 6$ , which makes the Fe moment decrease up to  $2.45 \mu_B$ ; the collected statistics (spin moments *vs.*  $N_c$ ) are presented in Figure 2B. Again we see a linear behaviour of the moment *vs.*  $N_c$ .

Next we turn to Fe clusters on Cu(001) and Cu(111) surfaces, for which we considered the same types of clusters as in the case of Ni. Since the Cu lattice parameter is slightly larger than the one of Ni, one might expect a lesser degree of hybridisation and therefore increased spin moments at the Fe atoms. Nevertheless, the moments are slightly lower, presumably because in the case of Ni the magnetisation of the substrate assists the spin polarisation of the cluster. The results for clusters on Cu(001) and on Cu(111) are shown in Figure 3A and 3B respectively. The result for the single adatom, showing again the highest moment, should not be taken literally: it is well known that magnetic impurity atoms in the bulk and on the surface of nonmagnetic hosts enter the Kondo regime at low temperatures, whence the spin moment shows quantum fluctuations and has a net average

(A) Moments in Fe clusters at Ni(111) surface

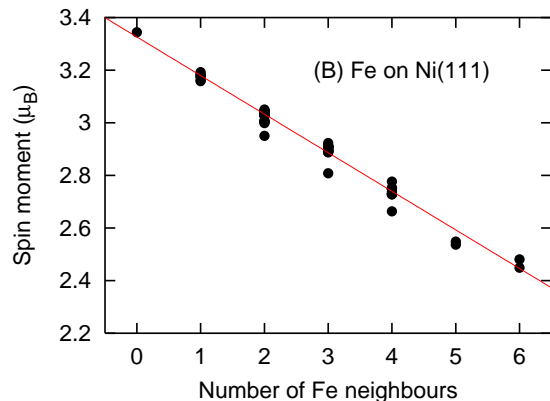
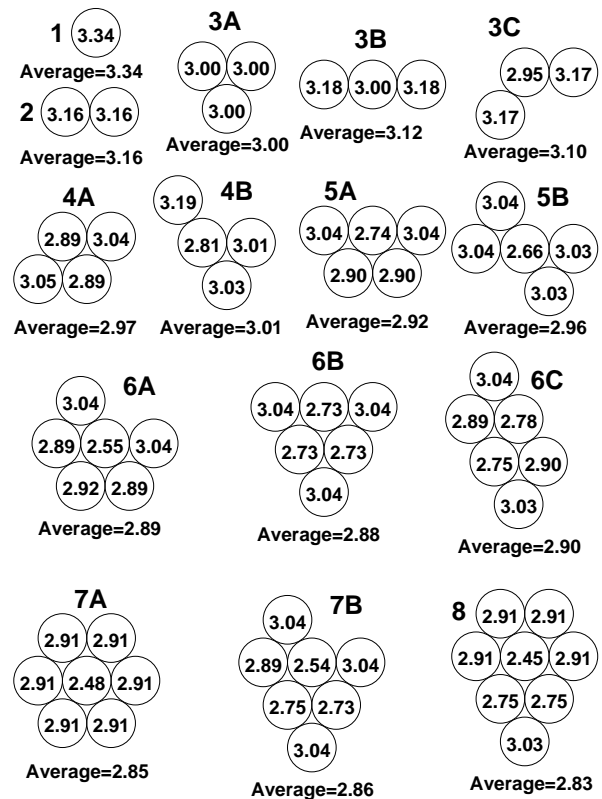


FIG. 2: A: Spin moments (in  $\mu_B$ ) of atoms in 15 different Fe clusters ranging from 1 to 8 atoms on the Ni(111) surface, and average (per atom) moments of the clusters (the clusters are viewed from the top, *i.e.*, all atoms lie on the surface). B: Linear trend for the atomic Fe spin moment as function of the coordination number of Fe neighbours.

of zero. This regime is not accessible by a mean field theory as the LSDA. Thus the result shown here for the adatom should be considered either as the trend of the LSDA calculation, or what one expects above the Kondo temperature. For magnetic clusters (dimers and larger) the quantum fluctuations of the moment are strongly suppressed and the Kondo temperature decreases drasti-

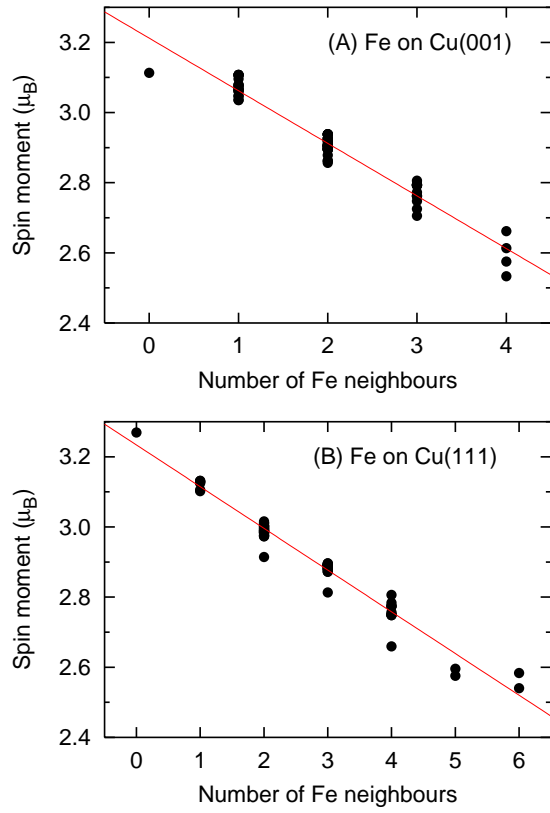


FIG. 3: Linear trend for the atomic Fe spin moment as function of the coordination in Fe clusters on Cu surfaces. A: on Cu(001), and B: on Cu(111).

cally with cluster size; thus the results given here for the clusters are realistic.

The linear dependence of the spin moments is again evident, except perhaps the result for the single adatom ( $N_c = 0$ ). A fit of the calculated data, using a linear equation of the form

$$M = -aN_c + b, \quad (1)$$

where  $M$  is the local spin moment, results in values for  $a$  and  $b$  given in Table I. We note that calculations on Fe nanostructures on Ag(001), reported for instance in Refs. [9] and [11] (using the KKR method), and [12] (using the SIESTA code), show a similar trend, although in these works fewer kinds of clusters are presented.

In summary, we have presented first-principles calculations of small Fe clusters on Ni and Cu (001) and (111) surfaces. The average (per atom) spin moments of the clusters are reduced with cluster size, mainly because the higher average coordination of the Fe atoms increases the hybridisation of the d states. The important parameter turns out to be the local coordination of each distinct Fe atom, irrespectively of the exact size or shape of the cluster. A linear relation of the coordination to the atomic spin moment has been found in a good approximation.

Surf.	$a(\mu_B)$	$b(\mu_B)$
Ni(001)	0.17	3.29
Ni(111)	0.15	3.33
Cu(001)	0.15	3.21
Cu(111)	0.12	3.23

TABLE I: Parameters  $a$  and  $b$  from the linear fit of the spin moment according to Eq. (1).

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